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IR Properties of Ge-doped CH - a continuation....

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Subject: *IR Properties of Ge-doped CH - a continuation....*

Summary

We have reexamined Ge-doped CH and have found that the material is more reactive to air than previously understood. The Ge-doped material as formed shows by IR the presence of a Ge-H linkage that oxidizes rapidly, giving rise to a significant OH absorption. This broad peak impacts IR layering wavelengths of interest.

Introduction.

In a previous memo[1] we provided our first look at the IR spectrum of Ge-doped CH. The primary question addressed was whether the Ge-doping interfered with the IR transmission at wavelengths of interest for IR enhanced DT layer formation. By comparing with undoped CH we identified Ge related peaks in the 18 μm thick 0.6 atom % doped sample, and came to the tentative conclusion that Ge doping did *not* modify the IR transmission in regions that we were interested in. We did note, however, that there was a little more absorption in the OH region (3700 to 3200 cm^{-1}) which impacted somewhat our estimate of the extinction coefficient in the neighborhood of 3.16 μm. Our opinion was that this was due perhaps to the use of a different coater. We promised to explore it further. We have, and the results are quite surprising (and discouraging)! The search for the ideal ablator has gotten more complicated.

Samples and measurements.

Four ~20 μm thick coatings were made on salt disks, at 0.0, 0.5, 1.0 and 2.0 atom % Ge. These are nominal levels based on experience with dopant gas flow rates, XRF analysis of the actual levels has not yet taken place. Table I gives the sample names used in this memo and the actual thicknesses.

Table I. Sample information

sample ID	atom % Ge	thickness
Ge00	0.0	17.9 μm
Ge05	0.5	20.5 μm
Ge10	1.0	20.8 μm
Ge20	2.0	23.3 μm

[1] Bob Cook, Abbas Nikroo, Mitch Anthamatten, Steve Letts, "*1) IR spectrum of Ge-doped CH ($\sim CH_{1.3}Ge_x$) and 2) New evaluation of ε(λ) for CH,*" February 28, 2003, copy available from Bob Cook.

The IR spectrum was taken a few minutes after each sample was removed from the coater. The samples were then left exposed to ambient conditions and the spectra retaken at various time intervals. For each sample, data for the sequential time measurements are indicated by appending t1, t2, t3,... to the sample name. The values of the elapsed time for each measurement for each sample are shown in Table II, where time is measured from the time the samples are first exposed to atmosphere.

Table II. Measurement time information, times in minutes.

time index	Ge00	Ge05	Ge10	Ge20
t1	2	10	7	1
t2	16	1428	17	10
t3	55	7061	25	22
t4	93	21594	40	35
t5	162		72	80
t6	187		135	150
t7	5633		417	193
t8	9939		651	267
t9			1430	390
t10			6354	408
t11			20184	13274

Assignment of peaks.

Shown in Figure 1 are the initial (at time t1) baseline corrected absorbance (prefix "ca") spectra[2] for the four samples. In Figure 1a we see that the most dominant Ge concentration dependent feature occurs between 1000 and 500 cm^{-1}, and is likely some sort of C-Ge stretch. As reported in our previous memo, the pure tetramethylgermane dopant has a strong absorption at about 800 cm^{-1}. Though interesting, the assignment of these and other related peaks are not our focus. Moving to the bottom (Figure 1b) expanded set of spectra there are two important features to note. First the concentration dependent peak just above 2000 cm^{-1} is the Ge-H stretch as we suggested in our February 28, 2003 memo. This assignment was made because a) silane (SiH_4) also shows a sharp peak here and b) tetramethylgermane, $Ge(CH_3)_4$, our dopant source, which has no Ge-H bonds, shows no peak here. Since releasing that memo we have learned[3] that GeH_4 has vibrational modes at 2106 and 2114 cm^{-1} and as noted above there is concentration dependence. As we will show shortly, this peak is not just a curiosity, but rather has some important time dependence. Last, note the spectra between 3600 and 3200 cm^{-1} where the OH stretch is manifest. We saw this slight enhanced absorbance in the previously reported work, but felt it was probably due to a coater variation, in part because it did not seem reasonable that Ge doping could affect the OH stretch region. However the current results lead us to rethink this. Before we proceed note that the magnitude of the OH absorbance shown in Figure 1b is *inversely* proportional to the Ge doping level, a curious result if in fact the enhanced absorption relative the undoped sample is related to the Ge-doping. As described below in some

[2] Baseline correction was the average value of the uncorrected absorbance between 5500 and 4600 cm^{-1}.
[3] Information supplied by Barry McQuillan, General Atomics.

detail, it turns out that the magnitude of the enhancement in the OH stretch is dominated by time dependence rather than concentration dependence, and as seen in Table II the initial measurements were made later on the 0.5 atom % sample than on the others.

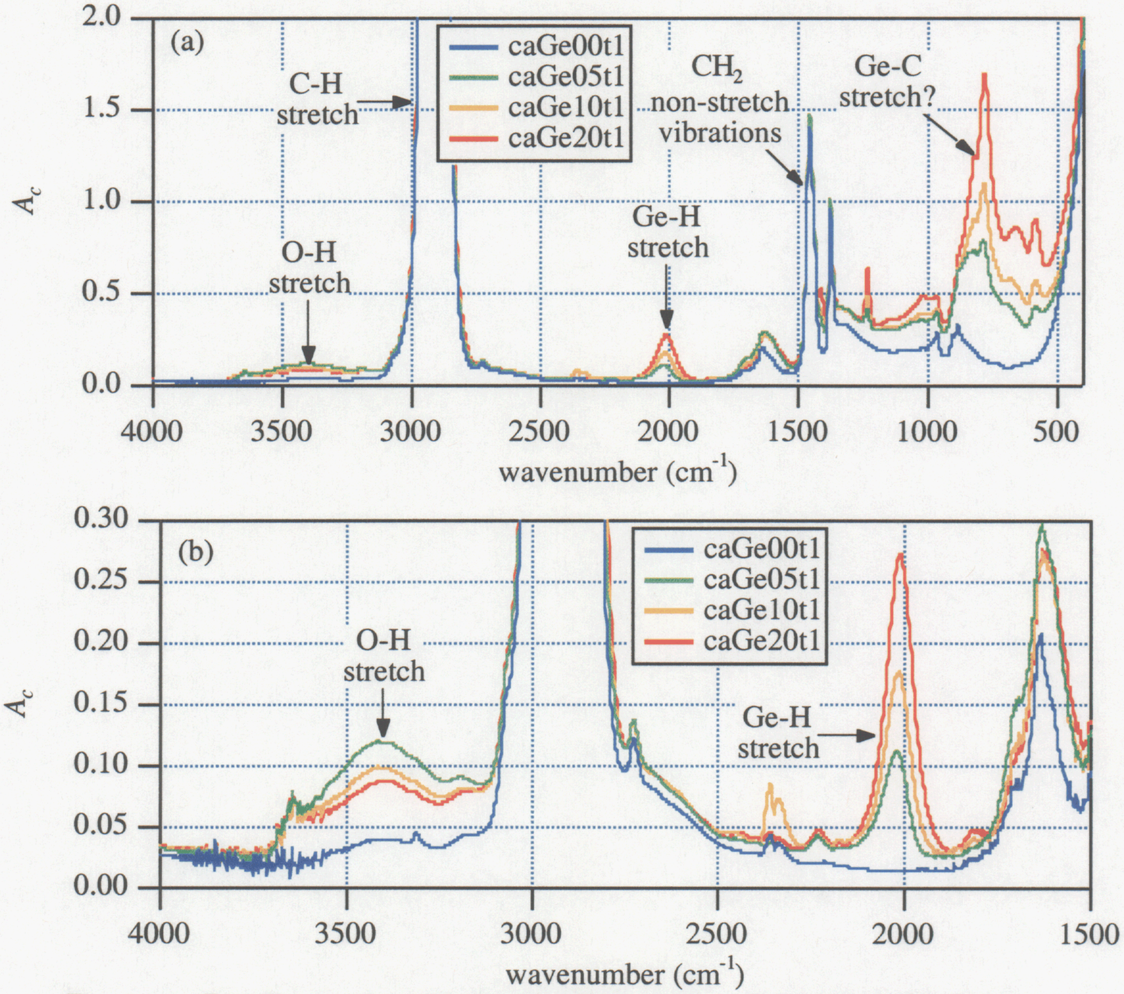

Figure 1. Baseline corrected absorbance spectra of the initial (earliest time) measurement on each sample. The bottom plot (b) is an expansion of the full spectra at the top (a).

Time dependence.

In Figure 2 we show the IR time dependence of the undoped and 1.0 atom % Ge doped samples over the range from 4000 to 400 cm^{-1}. Although the timing is different for the two samples it is clear that the Ge-doped sample absorbance is changing much more rapidly than that of the undoped sample. Our primary interest is in the OH stretch centered between 3600 and 3200 cm^{-1} because its low frequency shoulder effects the absorptive characteristics of the sample at wavelengths of interest for IR enhanced layering. In Figure 3 I have focused on the O-H and the Ge-H stretch. In the case of the Ge-H absorption I have reevaluated the baseline in the region of the peak so that the

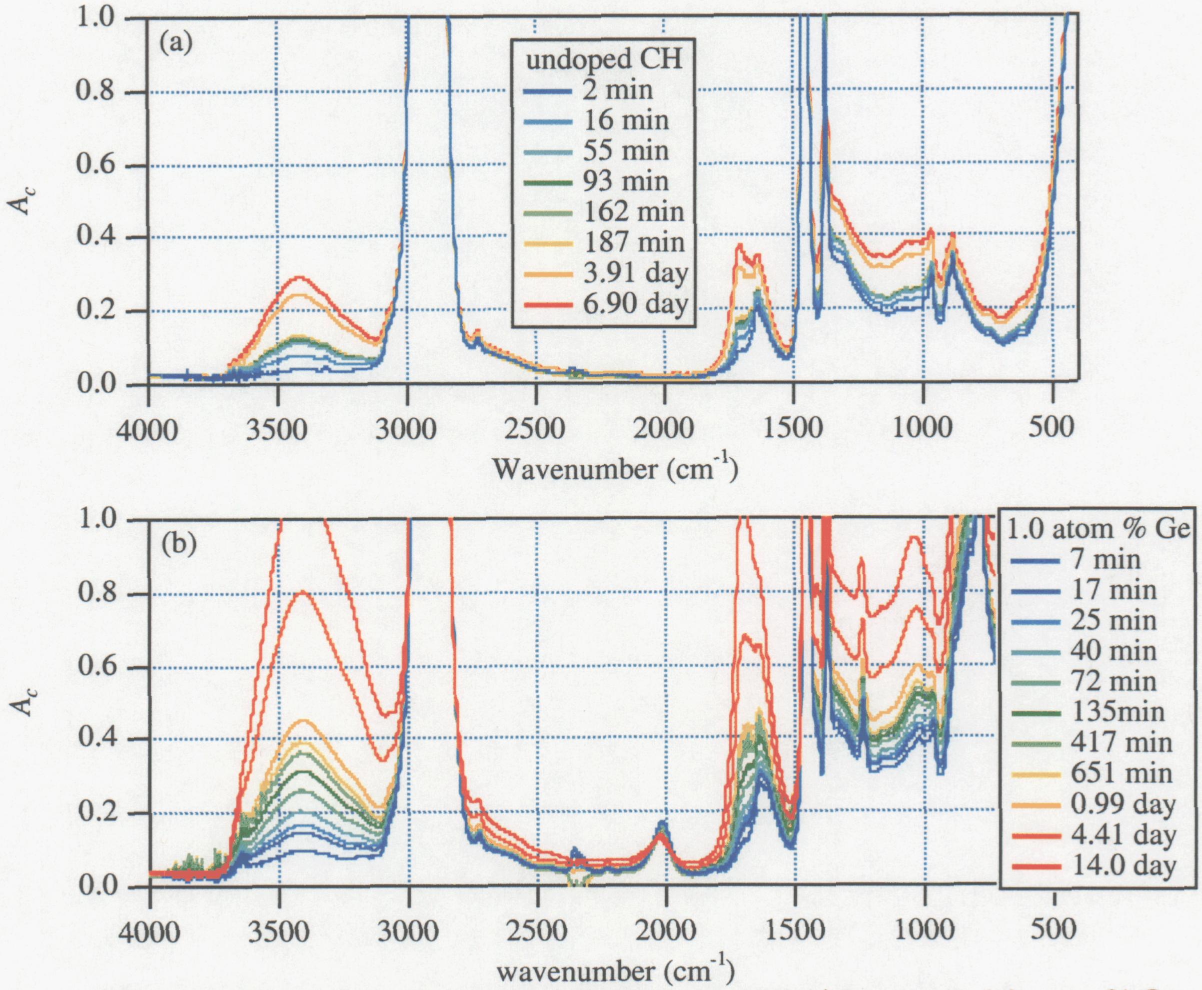

Figure 2. Time evolution data. a) Top is undoped, b) bottom is 1.0 atom % Ge.

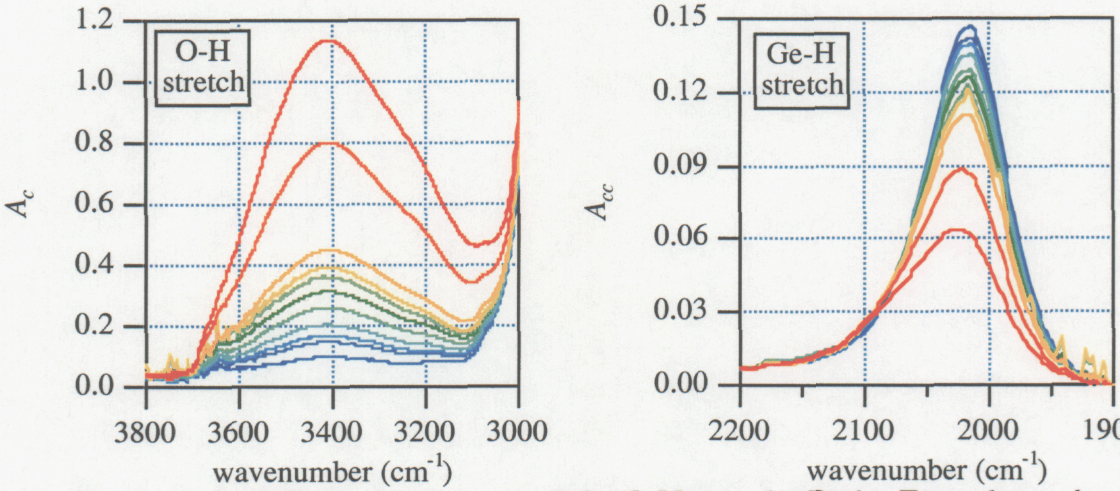

Figure 3. Left: Time dependence of the O-H stretch. Right: Time dependence of the Ge-H stretch. Color scale is the same as in Figure 2b.

absorbance at 1900 cm^{-1} is zero, and labeled this recorrected absorbance A_{cc}. The important feature is that the Ge-H stretch absorption is decreasing with time as the O-H stretch grows.

It is tempting but frustrating to try to identify the mechanism and or the kinetic order of the process. Cotton and Wilkinson[4] note that germane (GeH_4) oxidizes rapidly, though not as rapidly as silane (SiH_4) which combusts spontaneously in air. They also note that GeH_4 is quite resistant to hydrolysis compared with SiH_4, in fact they state that GeH_4 is stable in 30% NaOH!! Thus in the absence of other data it seems unlikely that ambient water vapor is playing a role, however this should be experimentally confirmed. In a simplistic picture in which all Ge-H sites are the same one would expect the observed rate of the reaction to be first order in the Ge-H site number, giving rise to an exponential decrease in the Ge-H absorption intensity:

$$A_{\mathrm{Ge-H}}(t) = A_{\mathrm{Ge-H}}(0)\exp(-kt) \ . \tag{1}$$

However a plot of $\ln[A_{\mathrm{Ge-H}}(t)]$ vs. t is distinctly non-linear regardless of time scale as shown in Figure 4. Clearly from Figure 3 about 40% of the Ge-H moiety is stable over a 2 week period, yet 25% of it is lost in the first 10 hours, and perhaps 10% in the first hour. Clearly there must be a variety of Ge-H type linkages and environments, each with its own oxidation kinetics. Some may in fact be quite stable as the long time data suggests.

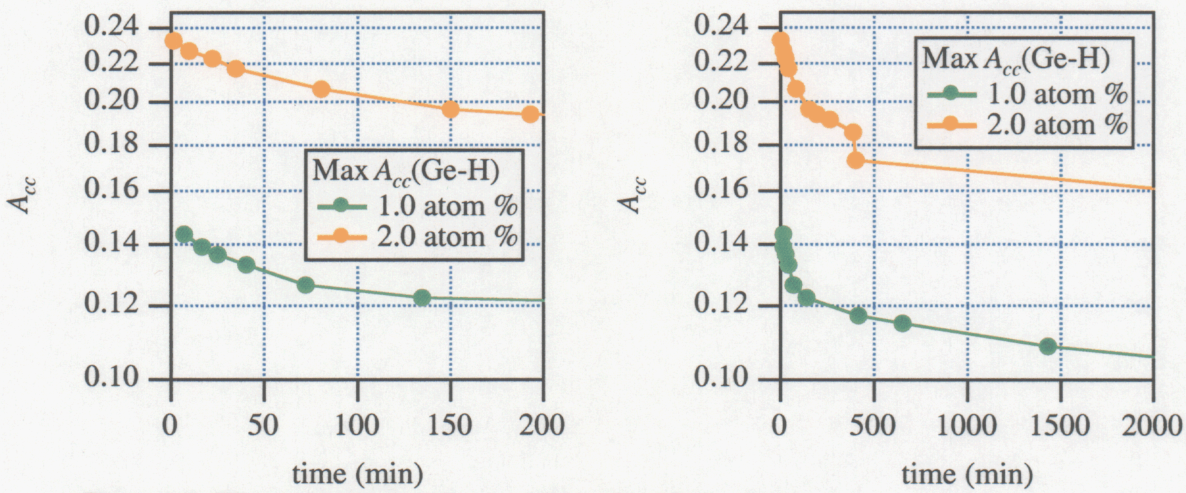

Figure 4. The time dependence of the Ge-H absorption.

The real problem, of course, is not the Ge-H absorption but rather that the oxidation of this linkage is correlated to a significant increase in the broad OH absorption, and this impacts the wavelengths that might be used for IR enhanced DT layer formation. In Figure 5 we show the absorbance of the OH stretch at its maximum

[4] F. A. Cotton and G.Wilkinson, *Advanced Inorganic Chemistry, 3rd ed.*, Interscience (New York) 1972, p. 318

(~3400 cm^{-1}) as a function of time. The plot on the left shows that the OH absorbance for the doped samples rises very rapidly compared to the undoped samples, and further the initial rise over the first hour seems fairly insensitive to dopant level.[5] The initial observation that the magnitude of the enhanced OH stretch in the "zero time" IR measurements (Figure 1) was inversely proportional to Ge concentration is explained completely by the fact that the initial measurement times for the 0.5, 1.0 and 2.0 atom % samples were 10, 7 and 1 minutes respectively. Although one can imagine Herculean efforts to limit air exposure, it is hard to imagine keeping it less than a few minutes, probably an hour or more is more realistic.

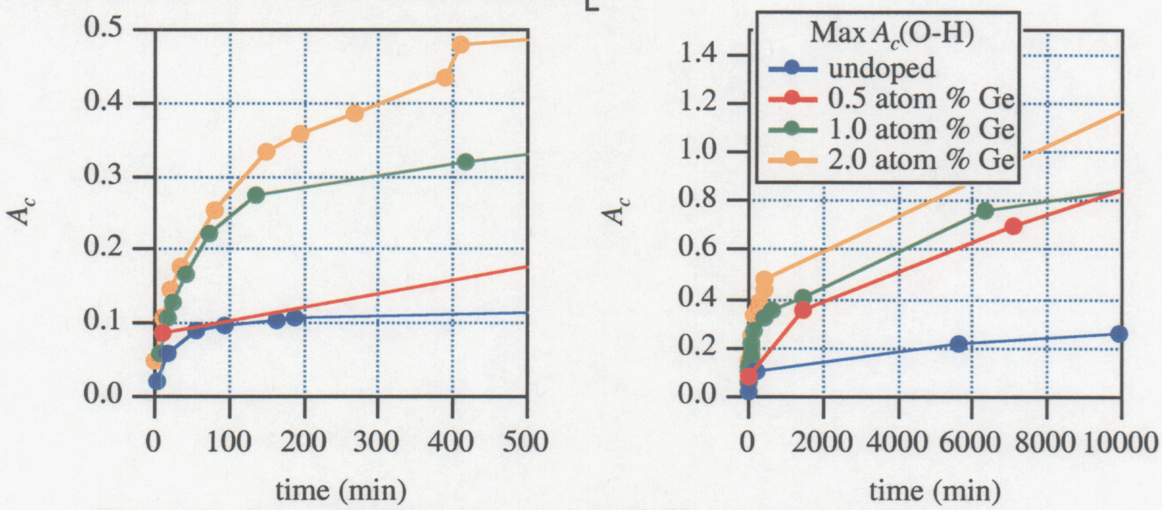

Figure 5. Corrected absorbance of the O-H stretch at its maximum position as a function of time.

If the OH absorption were narrow we would not have a problem since 3400 cm^{-1} is some distance from the region of interest for IR layering. However the absorption is very broad and clearly effects the extinction coefficients in the 3.16 μm area (about 3160 cm^{-1}, see Figure 1). In Figure 6 we plot the estimated[6] extinction coefficient at 3.161 μm as a function of time based on the current data. It is interesting that at least at short times the extinction coefficient is *independent* of the doping level (for doped samples). This is a result of the similar early time growth rates of the OH absorption for doped samples regardless of doping level as noted earlier. However what is most important is that this dopant effect on the OH absorption takes a marginal ablator (undoped CH) for IR layering and makes it markedly worse. I would certainly expect the same sort of enhanced oxidation for CD, though if the product is OD (rather than OH) the effect of the wavelengths of interest may be much less.

Work to be done.

As noted above we need to look at this effect for deuterated plasma polymer. In general the oxidation of deuterated material is of interest since one would expect to get O-D stretch absorption at perhaps 2400-2500 cm^{-1}, but some data has suggested that

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[5] The 0.5 atom % sample was the first studied and no short-term data was collected since we didn't expect to see this rapid rise. But the longer time data certainly suggests a similar short time rise.
[6] Estimated by dividing the corrected absorbance by the sample thickness.

even with CD one gets OH upon oxidation. I don't think we understand this and we need to. In any case Ge-doped CD needs to be looked at. The other factor that needs to be explored is the effect of pyrolysis on the rate of oxidation. Data yet to be written up clearly shows that the rate of oxygen uptake by undoped CH shells that have been through pyrolysis is markedly *reduced* compared to unpyrolyzed samples. One might expect a similar effect for Ge-doped materials, but this must be tested.[7] However if pyrolysis is part of the answer, we will need to pyrolyze full thickness shells which leads to significant darkening that may impact layer characterization.

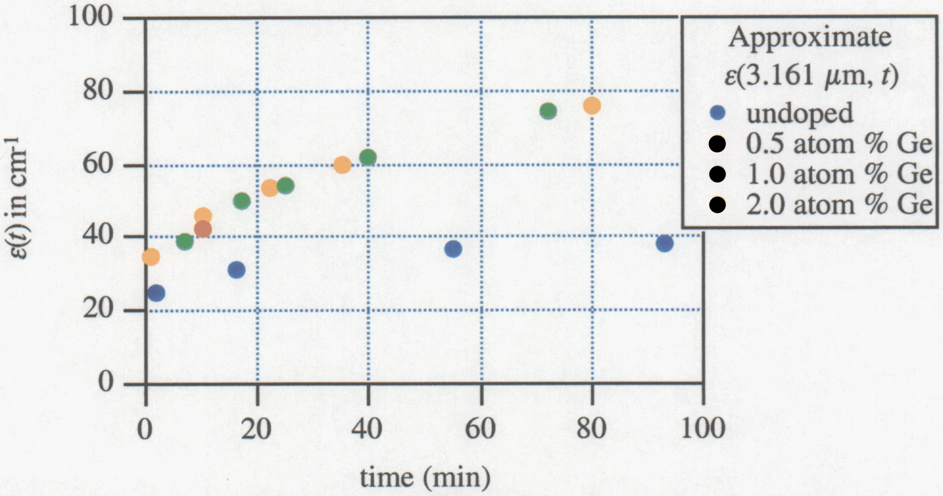

Figure 6. Estimated extinction coefficient as a function of air exposure time.

[7] There is some preliminary data that shows that pyrolyzed 0.5 atom % Ge-doped CH shells pick up oxygen more slowly than unpyrolyzed and undoped CH shells. The effect of pyrolysis on oxygen uptake is the subject of a separate ongoing study.